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# PHOTO-IONIZATION OF CÆSIUM VAPOR BY ABSORPTION BETWEEN THE SERIES LINES

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## ABSTRACT

Measurements by the space-charge method have been made on photo-ionization resulting from a small continuous absorption between the series lines. Results are expressed in terms of relative sensitivity  $I(\lambda)/I(3,200)$ . At 0.064 mm pressure  $I(\lambda)/I(3,200)$  increases from 0.0003 at 3,750 Å to 0.07 at 3,250 Å.  $I(\lambda)/I(3,200)$  increases roughly as the square root of the pressure throughout this wave-length range. On the short wave length side of 3,500 Å the effect decreases with increasing temperature of the vapor, the effect being reduced to half for a 70° rise in temperature. On the red side of 3,500 Å there is little, if any, temperature change. Results other than the temperature effect can be explained on the hypothesis that the absorption between lines is purely atomic as there is some line absorption far from the line center.

However, the temperature variation indicates a molecular origin and leads to an estimate of 0.26 electron volts for the work of dissociation of  $\text{Cs}_2$ . Other results can be qualitatively explained on the same hypothesis.

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## I. INTRODUCTION

Measurements of the photo-electric ionization of caesium vapor have shown that the photo-electric sensitivity is not limited to the region of continuous absorption beyond the principal series limit at 3,184 Å, but extends far into the region of line absorption to 3,888 Å. Spectral sensitivity curves of the ionization produced by a continuous spectrum dispersed by a monochromator show that most of this effect is in peaks at the positions of the absorption lines with a small background between the lines. A recent paper by the authors gives a quantitative study of the ionization at the lines.<sup>1</sup> The absorption responsible for the peaks is in narrow atomic lines of the order of

<sup>1</sup> Mohler and Boeckner, B. S. Jour. Research, 5, July, 1930 (RP 186). For brevity we will refer to this paper simply by this number.



0.01 A wide and ionization depends upon the collision of the excited atom produced by line absorption with a normal caesium atom during the life of the excited state. The probability of such a collision depends on the vapor pressure and is independent of the temperature. Results support a theory of Franck's that the excited atom and normal atom can unite to form a molecule ion.

The small background between peaks must be ascribed to a small absorption between lines. Published results indicate the magnitude of this absorption, assuming that it is truly continuous. In paper No. 186, Figure 4, curve 1 obtained in caesium vapor at 0.14 mm pressure shows a background between the peaks at 3,612 and 3,477 A of about 0.05 times the peak height. The effective width of the monochromator slits was 40 A, while the absorption lines at this pressure gave nearly complete absorption over 0.04 A. Assuming an equal probability for ionization at the lines and between the lines, then the absorption exponent between lines must be about  $5 \times 10^{-5}$ . At lower pressures much higher sensitivity can be obtained and absorption of less than  $10^{-7}$  of the incident light can readily be detected. Photoionization measurements offer the possibility of studying phenomena far beyond the range of more direct methods, but an obvious limitation is set by the low resolving power of monochromators. This can be partly remedied by using in addition to the continuous spectrum selected line sources having isolated strong lines in the spectrum range involved. The mercury arc lines near 3,650 and 3,340 fulfill this requirement. Earlier work indicates some difference of opinion as to whether these lines give any effect. Foote and Mohler<sup>2</sup> give a curve showing a slight effect at 3,340 A while Little<sup>3</sup> observed sensitivities at 3,340 and 3,650 of 0.05 and 0.03 of the sensitivity at 3,130 in saturated vapor at 166° C., but ascribed this to scattered light from the 3,130 line. In the following work relative sensitivities of about 0.006 and 0.003 are observed at this pressure which is not inconsistent with either of the earlier observations.

The following experiments have been guided by the recognition of two possible origins for the absorption between lines. It may be purely atomic since the absorption in a line is not limited to the small width commonly spoken of as the line width and the residual effect to be expected at 50 or more Angstroms from the line center may well be measureable by our methods. On the other hand, a small concentration of caesium molecules may give rise to this background. It will be seen that the experiments designed to distinguish between these two hypotheses lead to conflicting results. These experiments cover the spectral distribution of the background absorption and its variation with vapor pressure, temperature, and the addition of foreign gases. On the atomic hypothesis we would expect little temperature effect while the concentration of unstable molecules would change greatly. The theories lead to different laws for the variation with caesium pressure. In another paper the authors<sup>4</sup> describe the modifications in ionization by line absorption produced by foreign gases. The gas modifies the ionization by its effect on the lives of the excited states and the reduction of a peak height in the presence of nitrogen or hydrogen is characteristic of the excited state concerned.

<sup>2</sup> Foote and Mohler, *Phys. Rev.*, **26**, p. 195; 1925.

<sup>3</sup> Little, *Phys. Rev.*, **30**, p. 109; 1927.

<sup>4</sup> Mohler and Boeckner, *B. S. Jour. Research*, **5** (RP208); August, 1930.



A similar reduction in the background near the peak would give evidence that the same excited state was involved.

## II. METHOD AND APPARATUS

### 1. METHOD

We have followed the experimental procedure described in earlier papers. Ionization is detected by the neutralizing effect of positive ions on a thermionic current limited by electron space charge. The dark current is balanced out and the current change produced by radiation is measured on a sensitive galvanometer. A limit on the attainable sensitivity is set by random fluctuations apparently produced by electro-magnetic disturbances of unknown origin and variable magnitude. The ratio of current change to ion current ranges from  $10^4$  to  $10^6$  depending on operating conditions. All observations consist of relative measurements in terms of some standard wave length near the series limit. These can be reduced to an absolute scale on the basis of published results.<sup>5</sup> The absorption coefficient per atom is  $1.85 \times 10^{-19}$  for the 3,130 mercury line,  $2.3 \times 10^{-19}$  at the limit, 3,184 Å; and about the same at 3,200 Å.

### 2. THE SPACE CHARGE TUBE

Various tubes used in this work follow the general design described before. A wire cathode is near the axis of a cylindrical anode which electrically incloses it, and light is admitted through a slit in the end or side of the anode. The caesium is kept in a side tube, and in operation the body of the tube and the side tube are heated by separate heaters so that the vapor pressure and temperature can be controlled independently. In one tube a third heater around the anode chamber made it possible to heat this part of the tube far above the window temperature to avoid discoloring the window.

### 3. LIGHT SOURCES

A 400-watt Mazda projection lamp served as a continuous spectrum source. Figure 2 of paper No. 186 gives the spectral intensity distribution in quanta per second obtained with our monochromator. It increases about fortyfold in the range 3,150 to 3,800 Å.

A 120-volt quartz Uviarc served as a mercury line source. To reduce scattered ultra-violet light a thick plate of pyrex glass was placed near the exit slit of the monochromator. By further reducing the 3,130 Å light with wire screens of 6 per cent transmission, the effect of this line was made comparable with the 3,340 and 3,650 Å lines. The resulting intensity ratio of 3,130 to 3,340 and to 3,650 was assumed to be 1 to 22 and 1 to 510. An inverted *u* quartz arc containing a mercury cadmium alloy gave the mercury 3,341 line and the unresolved lines 3,261 and 3,253 in the ratio of 2.5 to 1.

The Bausch & Lomb monochromator with both slits, 0.1 mm wide gives a peak about 60 Å wide at the base and nearly triangular in shape. Slits as small as 0.03 mm were used, but did not give a proportional increase in resolving power because of imperfect adjustment.

<sup>5</sup> Mohler and Boeckner, B. S. Jour. Research, 1 (RP3), p. 303; 1929.

## III. RESULTS

## 1. IONIZATION AS A FUNCTION OF WAVE LENGTH

Figure 1 shows on a large scale the ionization between lines as observed with a Mazda lamp at a caesium pressure of about 0.06 mm. It is a composite curve made up of observations with different slit widths. Table 1 gives values of the effect per unit radiation flux relative to the effect at 3,200 and to the line peaks and includes values based on measurements with mercury and cadmium lines. The small peak at 3,446 Å falls within 1 Å of the third principal

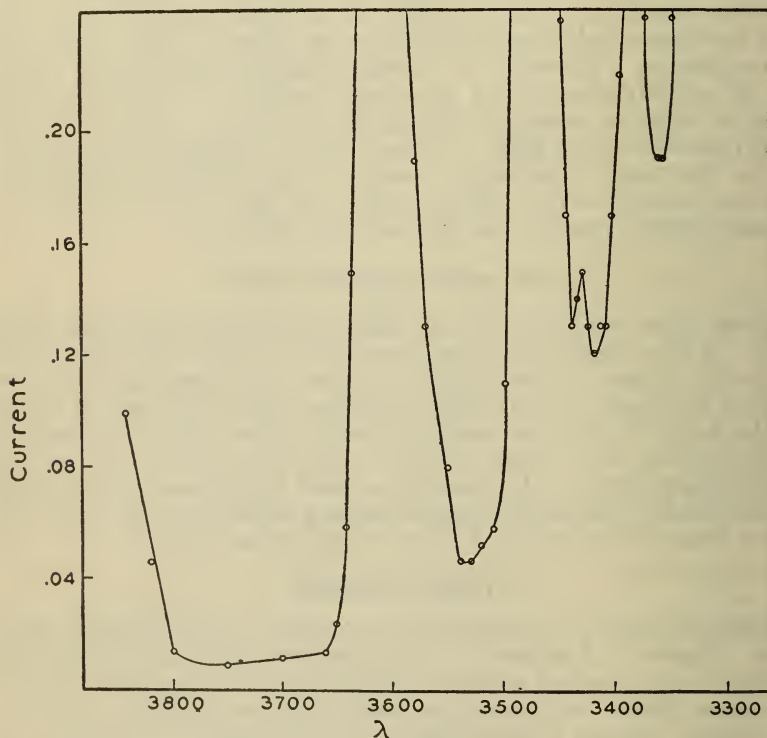


FIGURE 1.—Ionization as a function of wave length in Cs at 0.064 mm pressure

On the scale of ordinates the effect at 3,200 Å is 1.

series doublet of potassium. It was relatively strong at high pressures and at higher temperatures. Our experiments do not set definite limits to the background except that on the red side of 3,888 it was too small to measure.

In connection with the above, some absorption spectra obtained by Bevan in caesium vapor may be mentioned. These show that the absorption between the higher series lines remains small relative to the atomic absorption at the limit even at much higher pressures than those used here.<sup>6</sup>

<sup>6</sup> Bevan, Proc. Roy. Soc. A., 83, p. 421; 1910.

TABLE 1.—Relative amounts of ionization between absorption lines in *cæsium* at 0.064 mm pressure

$\lambda$ radiation	$\lambda_0$ Cs lines	I ( $\lambda$ )/I ( $\lambda_0$ )	I ( $\lambda$ )/I (3,200)	Source
3,750	3,612	0.0053	0.00027	Continuous.
3,700	-----	.0065	.00041	Do.
3,660	-----	.0076	.00054	Do.
3,650	-----	-----	.00047	Hg arc.
3,540	3,477	.030	.0032	Continuous.
3,510	-----	.037	.0045	Do.
3,420	3,398	.09	.0165	Do.
3,360	3,347	.165	.035	Do.
3,341	-----	-----	.027	Hg arc.
3,261	3,256	}-----	.068	Hg-Cd arc.
3,253	3,246			

## 2. PRESSURE EFFECT

Measurements with a continuous spectrum at various vapor pressures showed a marked increase with vapor pressure in the background relative to either 3,200 or to the peaks, but it was not feasible to get quantitative measurements over a wide pressure range.

Much larger effects could be obtained with the 3,340 and 3,650 lines of the mercury arc. Figure 2 shows the spectral distribution of ionization produced by mercury radiation passed through a plate of glass to reduce scattered ultra-violet light. There are peaks at the mercury lines and peaks at the *cæsium* lines. The latter come from a continuous background in the arc radiation, and the former from continuous absorption in the *cæsium*. The two effects are not completely resolved, but are readily separated graphically.

Figure 3 gives some observed ratios of the effect at 3,340 and 3,650 Å to that at 3,130 plotted against the square root of the pressure. Some uncontrolled factor made it impossible to reproduce results on the pressure variation within the range of precision suggested in the curves of Figure 2. The absolute sensitivity ratio is obtained by multiplying ordinates of Figure 3 by  $4.5 \times 10^{-2}$  for 3,340 and by  $2.0 \times 10^{-3}$  for 3,650. The change in continuous background with pressure at other wave lengths is comparable with the change at 3 650 and 3.340.

## 3. TEMPERATURE EFFECTS

During the course of measurements of the pressure effect with the mercury arc wide variations were found in the effect of the 3,340 line as compared with 3,650. The cause was finally found to lie in a large temperature coefficient of the ionization by the former line and to the fact that the furnace temperature had not been kept constant from run to run. Measurement showed that the effect at 3,340 was cut in half by a 70° rise in temperature.

Figure 4 shows a plot of  $\log TI(\lambda)/I(3,130)$  against  $1/T$ . The points at the higher temperatures were obtained by superheating the ionization chamber while many of the lower points were obtained by changing the temperature of the whole tube.

Measurements with the cadmium mercury arc were also made, using the unresolved Cd lines 3,252 and 3,261, and the 3,341 mercury



line. The lines at 3,260 and at 3,341 were found to show about the same temperature variation.

By use of the Mazda lamp, it was possible to locate spectral limits of the temperature effect. Figure 5 shows two spectral distribution curves obtained at 320° and 220°, the caesium pressure being kept at 0.06 mm. The 3,650 Å and 3,550 Å regions are seen to have no temperature effects, while at 3,440 and 3,360, there are large effects,

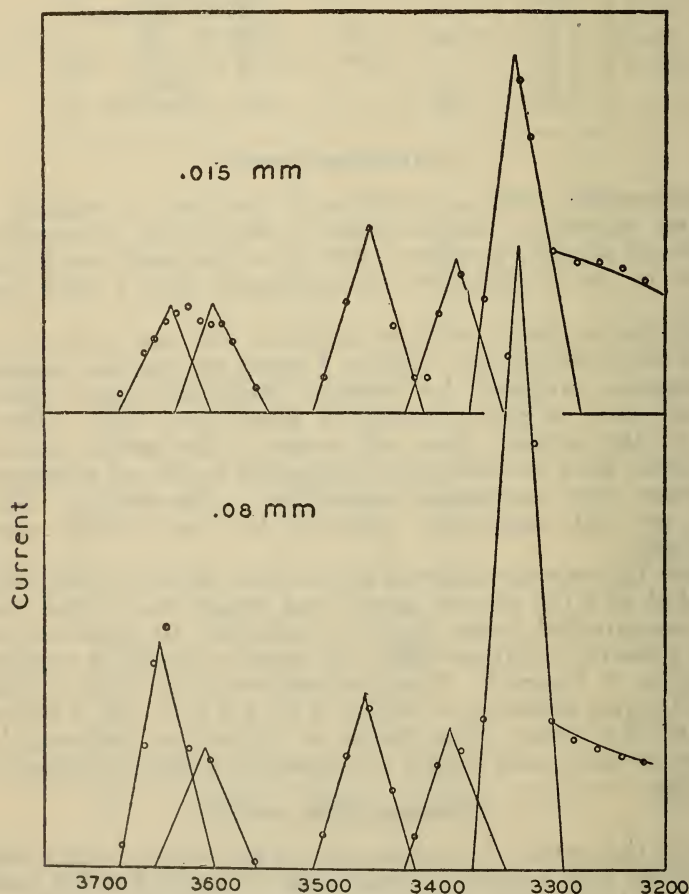


FIGURE 2.—Ionization produced by mercury arc radiation  
The two extreme peaks are at the position of mercury lines, the others at caesium lines.

somewhat smaller, however, than those obtained with the Hg arc in the same wave-length region.

#### 4. EFFECTS OF FOREIGN GASES

Figure 6 shows plots of the background with 2 mm of nitrogen and with no foreign gas in the space charge tube. The background at all wave lengths is quenched. Table 2 gives values of the quenching ratio for both the series lines and the background and it is seen that they are approximately the same.

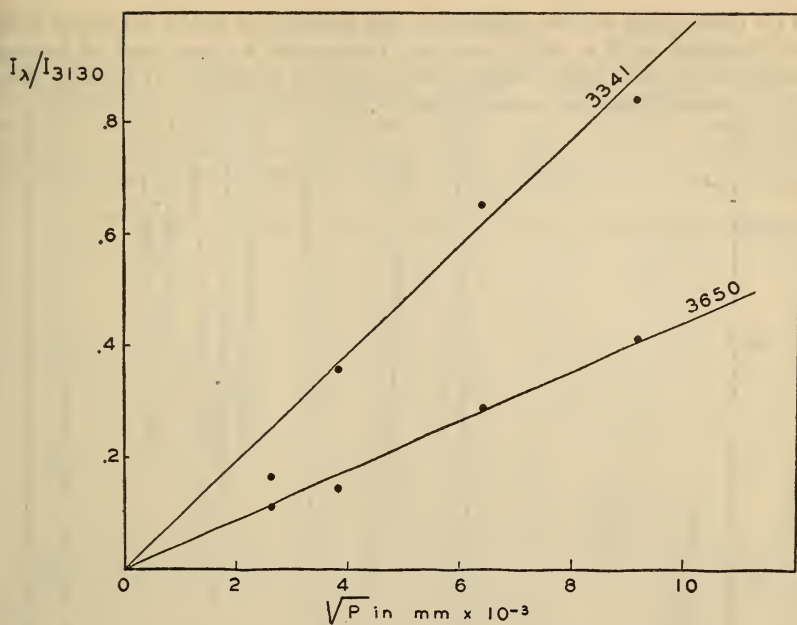


FIGURE 3.—Ionization as a function of pressure

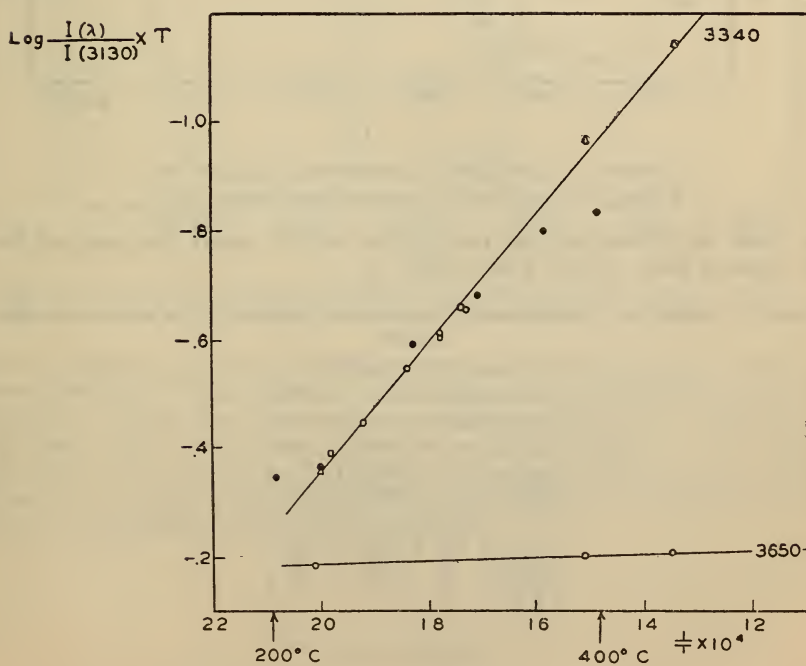


FIGURE 4.—Variation of ionization with temperature

The quenching of the effects of the 3,340 and 3,650 mercury lines was obtained with a tube that had developed a good deal of foreign gas (probably  $H_2$ ) after sealing off from the pumps. It is seen here

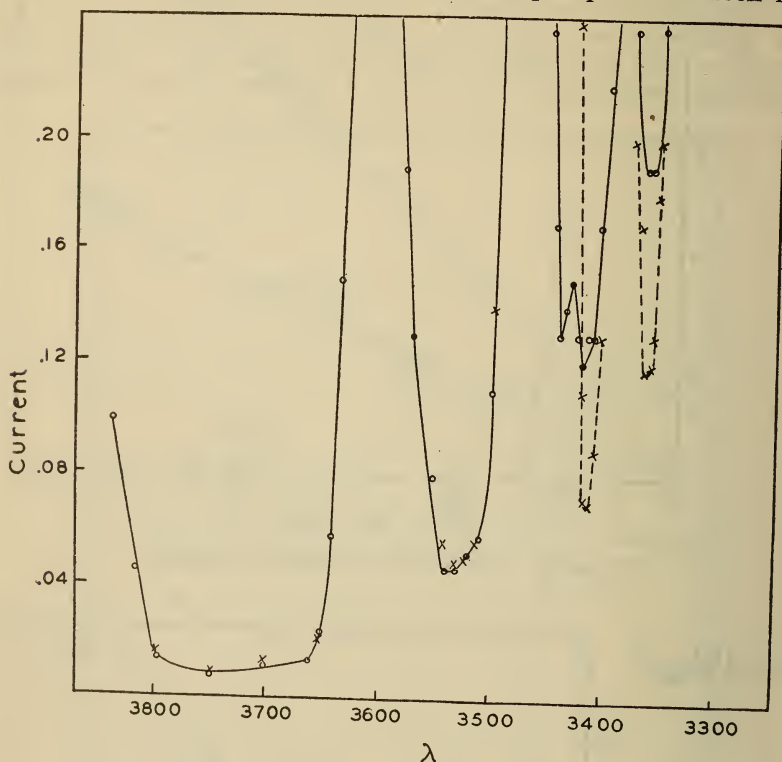


FIGURE 5.—Ionization of caesium vapor at 0.06 mm  
Full line and circles at 220° C.; broken lines and crosses at 320° C.

also that the quenching for the background is about the same as for the caesium lines at 3,612 and 3,347 Å.

TABLE 2.—Reduction of ionization by foreign gas. Ratio of effect with gas to effect without

2 mm OF NITROGEN			
Background		Lines	
Wave length	Ratio	Wave length	Ratio
3,750	0.21	3,612	0.18
3,700	.18	3,477	.20
3,540	.34	3,398	.24
3,430	.25	3,347	.29
3,360	.37		

UNKNOWN GAS			
3,650	0.30	3,612	0.29
3,340	.45	3,347	.52

## IV. DISCUSSION

We shall consider two possible origins of the absorption between lines which give rise to the photo-ionization. One possibility is that there are some caesium molecules which have a nearly continuous background of absorption between lines. The other possibility is that the absorption is purely atomic line absorption, for the absorp-

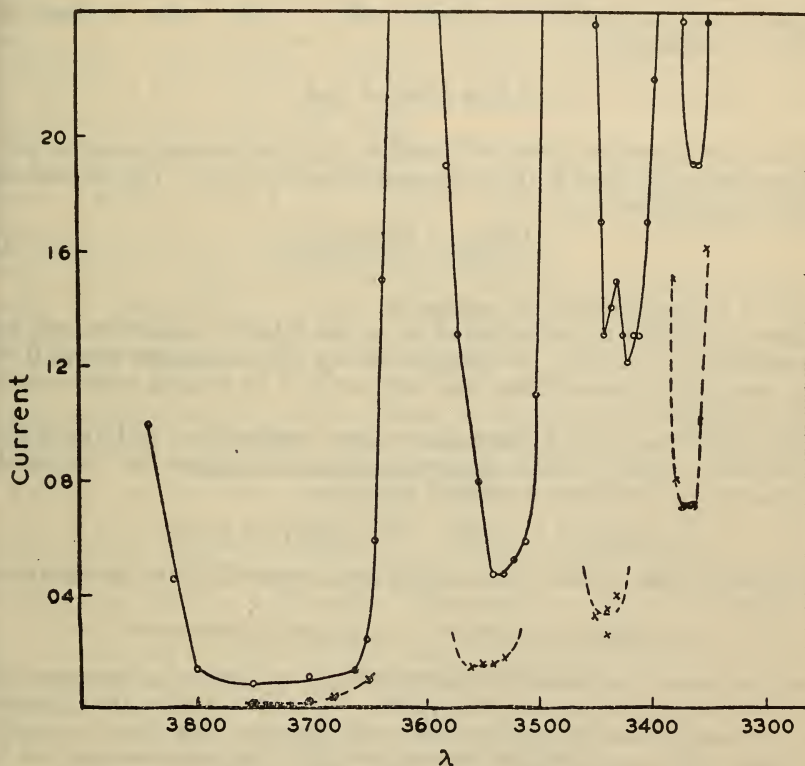


FIGURE 6.—Full line curve photo-ionization in pure caesium vapor. Broken curve with 2 mm of nitrogen added

tion of each line actually extends over an indefinitely large range of wave lengths. Both types of absorption are generally recognized to exist. In the atomic case it seems safe to assume that ionization will result from absorption with the same probability as for light coincident with the center of the line. For the molecular absorption there is no a priori basis for predicting the efficiency of ionization and several mechanisms must be considered.



## 1. ATOMIC ABSORPTION BETWEEN LINES

We shall assume <sup>7</sup> that the half widths of the lines are proportional to the square root of the pressure and that the absorption far from the line is given by

$$\frac{k(\lambda)}{k(\lambda_0)} = \frac{\Delta}{(\lambda - \lambda_0)^2} \quad (1)$$

where  $k$ 's are absorption exponents and  $\lambda_0$  is the center of the line while  $\Delta$  is defined by

$$k(\lambda \pm \Delta) = \frac{1}{2} k(\lambda_0)$$

Since  $\Delta$  is proportional to  $p^{1/2}$  and  $k(\lambda_0)$   $\Delta$  is proportional to  $p$  it follows from (1) that  $k(\lambda)$  is proportional to  $p^{3/2}$ . The measured relative ionization is

$$\frac{I(\lambda)}{I(3,200)} = \frac{E(\lambda_0) k(\lambda)}{k(3,200)} \quad (2)$$

where  $E$  is the efficiency of ionization.

Since  $k(3,200)$  is proportional to  $p$ , the relative ionization will be proportional to  $E p^{1/2}$ .  $E$  changes slowly with pressure above 0.01 mm., so relative sensitivity will vary as  $p^{1/2}$  in accord with results shown in Figure 3.

The 3,650 line is 33 Å from the nearest caesium line and the 3,341 line is 5.9 Å away. With absorption data from paper No. 186, with a pressure of 0.064 mm, equation (1) gives

$$k(3,341) = 1. \times 10^{-5} \quad k(3,650) = 1.1 \times 10^{-6}$$

Results of Table 1, with values of  $E$  from paper No. 186 in equation (2), give

$$k(3,341) = 4.8 \times 10^{-5} \quad k(3,650) = 2.8 \times 10^{-6}$$

The discrepancy between the computations can, perhaps, be expected from the nature of the approximations. The observation that foreign gas reduces ionization at the lines and between the lines in about the same ratio supports the conclusion that the same mechanism is involved. There is only one outstanding objection to the atomic origin of this ionization, the fact that the ionization is reduced at high temperatures.

## 2. IONIZATION CONSIDERED AS OF MOLECULAR ORIGIN

We assume that the molecules giving rise to the absorption are diatomic. They will exist in relatively low concentration which will depend on the temperature and pressure according to familiar thermodynamical relations. If  $n_1$  is the concentration of caesium atoms (proportional to vapor density),  $n_2$  the concentration of  $\text{Cs}_2$  molecules,  $Q$  the heat of dissociation of the molecules at temperature  $T$  and  $K$  the equilibrium constant of the reaction,  $\text{Cs} + \text{Cs} = \text{Cs}_2$ , then

$$\log K = \frac{Q}{2, 3 RT} + \text{const} \quad (3)$$

<sup>7</sup> Line widths at the vapor pressures used are determined by the caesium pressure. Experimental results (Waible, *Zeits. f. Phys.*, 53, p. 459; 1929) support the square root relation for the half widths. The experiments also give a basis for equation (1).

$$K = \frac{n_2}{n_1^2} \quad (4)$$

If we assume that  $I(3,130)$  is proportional to  $n_1$  and  $I(\lambda)$  to  $n_2$  (this assumes efficiency of ionization at  $\lambda$  is independent of density and temperature), we see that the form of equation (3) accounts for the observed temperature variation of the ionization at 3,340. (Fig. 4.) The slope of the line in Figure 4 gives a value for  $Q$  of 0.26 electron volts. Results shown in Figure 5 indicate that all the background on the short wave-length side of 3,500 Å can be ascribed to molecules with a similar value of  $Q$  while the background on the red side of 3,500 has a much smaller temperature coefficient and, hence, must have a different origin.

Equation 2 shows that the relative concentrations of molecules  $n_2/n_1$  is directly proportional to the pressure, while observations in Figure 3 indicate that  $I(\lambda)/I(3,130)$  varies more nearly as  $p^{1/2}$ . There remains the possibility that the probability of ionization of the excited molecule changes with pressure.

The absolute magnitude of  $n_2$  may be computed from relations similar to equation (3) based on statistical considerations.<sup>8</sup> For caesium at 0.1 mm. pressure and at about 300° C.,  $n_2/n_1$  lies between  $10^{-5}$  and  $10^{-6}$ , depending on the values used for  $Q$ , and other constants.

The estimates of 0.26 volt for the heat dissociation of  $\text{Cs}_2$  and 0.7 volt or more for  $\text{Cs}^+_2$  set certain limits to the regions in which photo-ionization is to be expected. The ionization potential of the atom is 3.87 volts. The minimum ionization potential of the normal molecule is  $3.87 - 0.7 + 0.26 = 3.43$  volts ( $\lambda = 3,600$  Å) while the minimum ionization potentials leading to high vibration states of the ion will range to  $3.87 + 0.26 = 4.13$  volts ( $\lambda = 3,000$ ). Excited neutral molecules which can spontaneously pass into the ion state can exist in the energy range 3.43 to 4.13 volts. The energy required to ionize a molecule in the normal electronic state, but in a high vibration state may be much as 0.26 volt less than that required for the normal molecule so that the range of photosensitivity will extend to beyond 3,800 Å as observed.

There is, however, an important difference between ionization on the red and violet side of the threshold (3,600 Å) for the normal molecule. Photo-electric absorption on the violet side involves normal molecules and will have a temperature coefficient appropriate to  $Q$  for the normal molecule. Photo-ionization by longer wave lengths depends on the concentration of molecules in high vibration states and will, therefore, have a much smaller temperature coefficient. The experimental observations of Figure 5 conform roughly to this prediction though the dividing line between high and low temperature coefficients is near 3,500 instead of 3,600 Å.

There are at least three possible mechanisms for the photo-ionization process: (1) Direct transition by absorption into the ion state, (2) transition into a discrete state of the neutral molecule with energy greater than 3.4 volts followed by a spontaneous transition into a molecule ion state of the same energy, and (3) transition into a dissociated state giving an excited atom which becomes a molecule ion by a subsequent collision. The most probable transition is the one

<sup>8</sup> Fowler, Phil. Mag., 45, p. 1; 1923.

which involves the least change in nuclear separation but this is not known for caesium.

The first and simplest process is ruled out by the fact that ionization is diminished by the presence of a foreign gas. This implies that some time must elapse between the absorption of radiation and the formation of an ion. Both the second and third processes involve a time interval during which a collision may destroy the excited state. The third process of ionization would give identically the same quenching by the foreign gas for the line peaks and for the background, the second a similar but not identical quenching. Another observation seems to favor the second mechanism. We have referred above to evidence that the probability of ionization of the excited molecule decreases with increasing vapor pressure. The results suggest that caesium vapor, as well as other gases, may quench ionization, and this is to be expected if the excited states are molecular and not atomic.

Whatever the nature of the ionization process may be, it must be highly efficient. This follows from the fact that the observed absorption between the caesium lines is small compared to that at the limit while the ionization itself is an appreciable fraction of that at the limit.

It may also be concluded that the absorption of the molecule is much greater than that of the atom, since the molecular ionization is comparable to the atomic even though the fraction of atoms associated must be extremely small.

### 3. CONCLUSION

Our discussion has led to an apparent paradox. Phenomena of ionization between lines can be explained by the assumption that the absorption is purely atomic except for the observed temperature variation of the ionization. The temperature variation clearly indicates a molecular origin of this ionization and all other phenomena are shown to be qualitatively in agreement with this. Results favor the hypothesis that absorption leads to a highly excited neutral molecule which spontaneously passes to a state of the molecule ion.

WASHINGTON, June 17, 1930.









